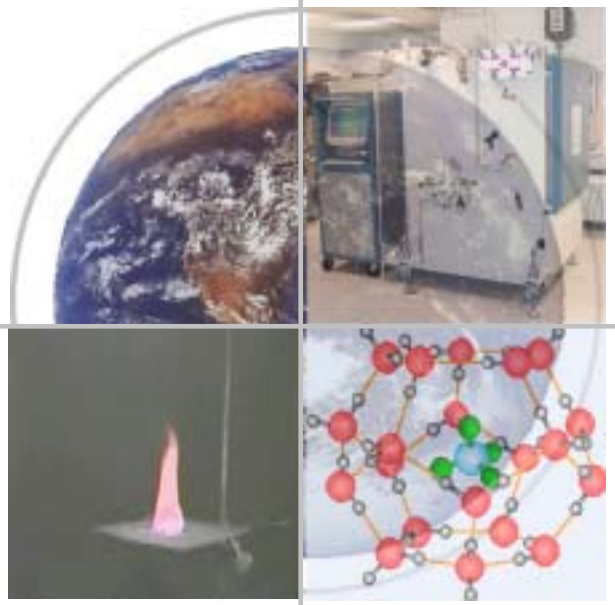
NETL/OST FY-2003 Gas Hydrate Research Program



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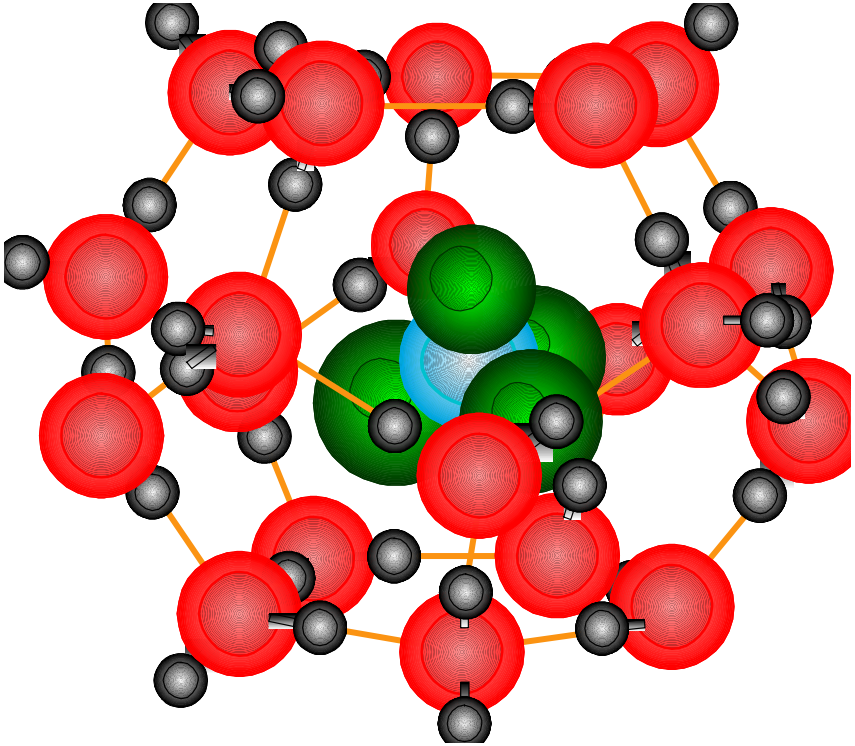
Computational Energy Sciences Focus Area
National Energy Technology Laboratory

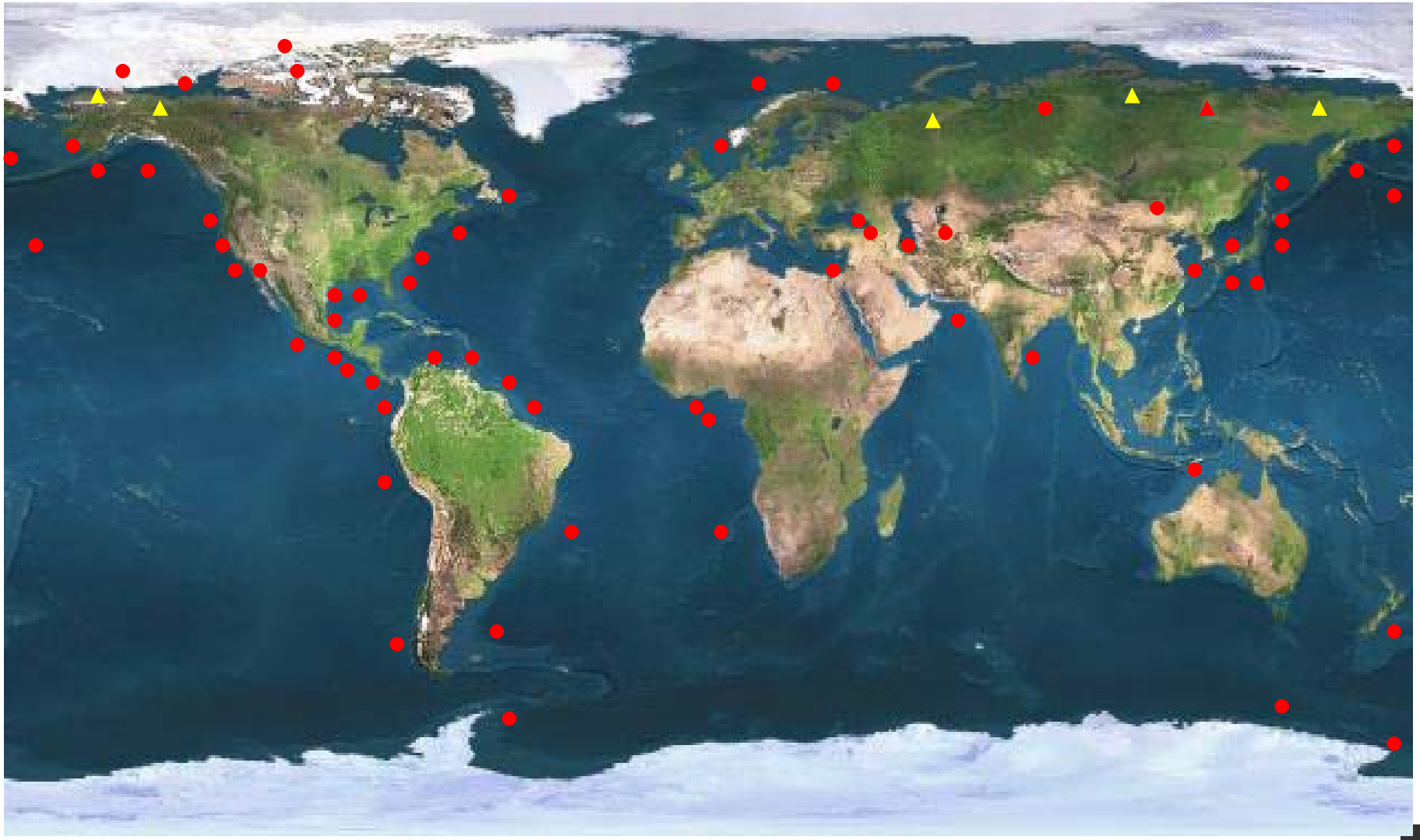
Mara Dean, Tom Mroz, and Robert P. Warzinski

What Are Methane Hydrates?

- The most abundant natural form of clathrate, a unique class of chemical substance in which molecules of one material (in this case, water) form an open solid lattice that encloses, without chemical bonding, appropriately-sized molecules of another material (in this case, methane).
- Methane hydrates are stable and occur naturally in deep-ocean and permafrost areas.



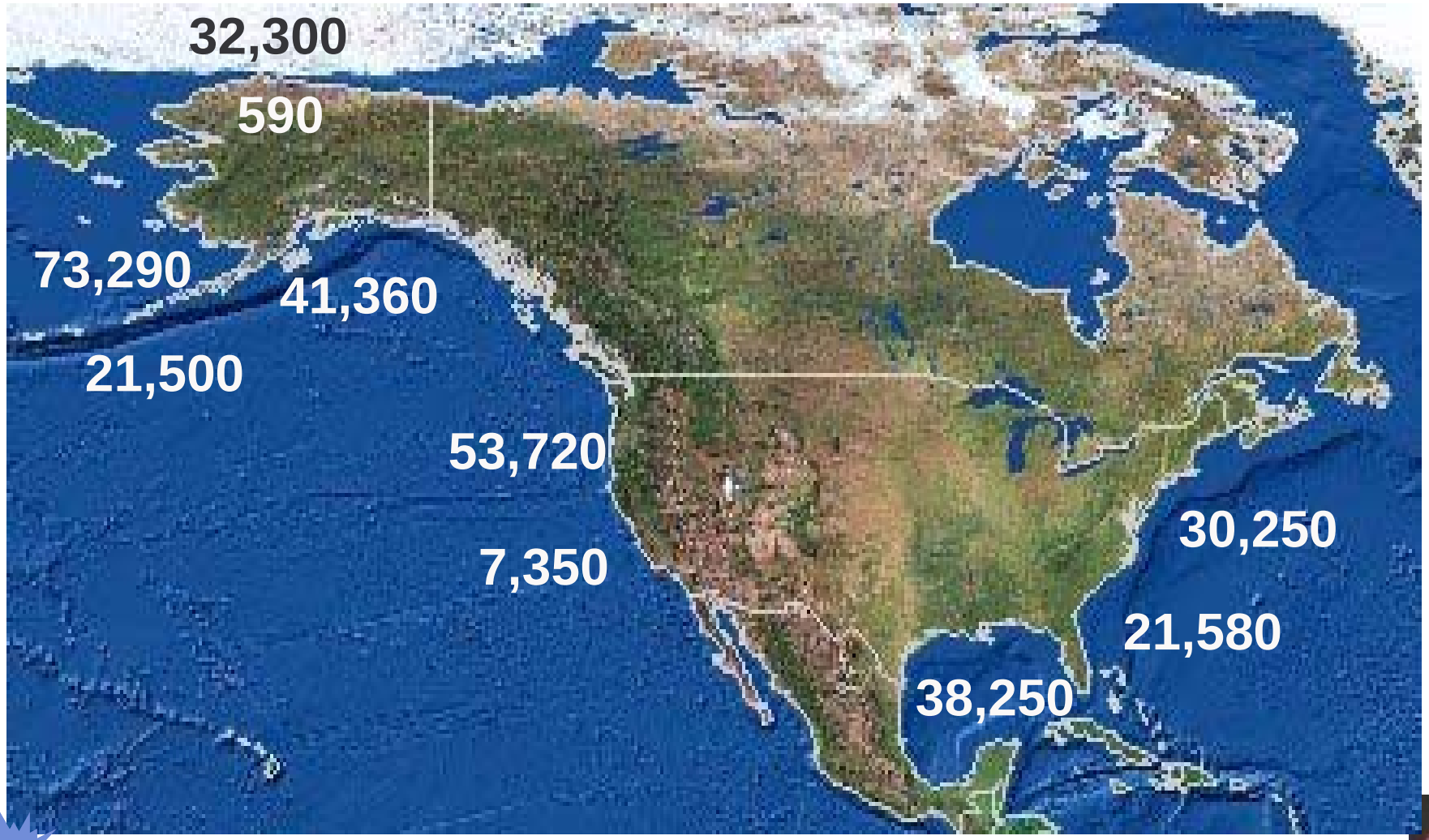
Global Gas Hydrate Locations



● Ocean Sediment △ Permafrost

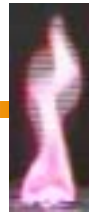
It is estimated that there is more organic carbon contained in methane hydrates than all other forms of fossil fuels combined

USGS Estimates of U.S. In-place methane contained within gas hydrates (Tcf)



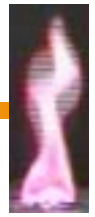
NETL/OST Gas Hydrate Research

- **Purpose: Compliment and supplement the external research in gas hydrates without duplicating research (find a niche…be the best).**
- **NETL/OST Research Areas:**
  - Modeling/Computational of Hydrates.
  - Physical Property Measurements.
  - Kinetics of Formation/Dissociation.
  - Enhancement in the Storage of Methane in Hydrates.
  - Development of real-time monitoring of gas hydrate wells during drilling.
- **NETL OST Research Team Principle Investigators:**
  - Mara Dean, Tom Mroz, Charles Taylor, Robert Warzinski



Reasons for OST Gas Hydrates Research

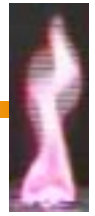
- A need exists to model reservoir behavior accurately in order to optimize production design The thermal properties of hydrate-bearing sediments strongly influence hydrate decomposition and therefore production.
- The thermal conductivity of the hydrate-sediment medium is one of the key knowledge gaps in developing gas hydrate simulators for resource recovery (conclusion of the 2001 MBARI Gas Hydrate Workshop).
- Kinetics of hydrate formation/dissociation under varying conditions not well understood.
- Field testing of hardware and software needed.



NETL/OST Major Methane Hydrate Laboratory Facilities

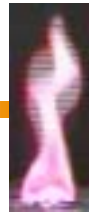
FY-02 Technology Transfer

- 8 Presentations (1 canceled due to 9/11 incidents).
- 1 Non-refereed Publication.
- 2 Refereed Publications.
- Organized and Chaired Gas Hydrate Symposium at 223rd National Meeting of the American Chemical Society in April 2002.
- Organizing Gas Hydrate Symposium at 2003 Spring National Meeting of the American Institute of Chemical Engineers.

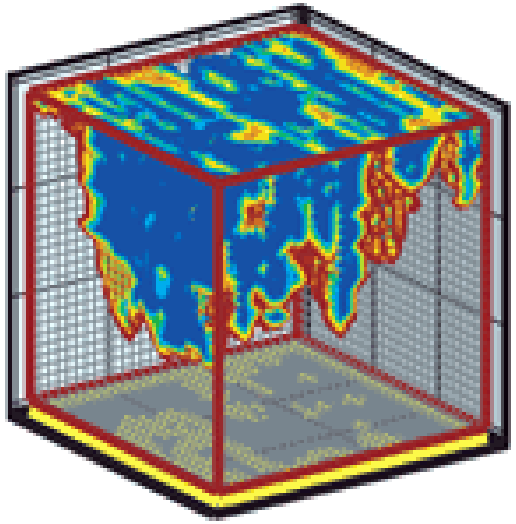


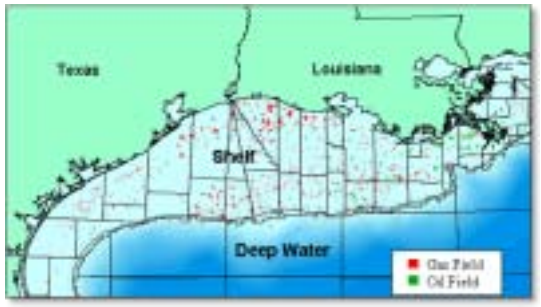
Modeling Reservoir Behavior During the Production of Gas From Hydrates

- **A need exists to simulate reservoir behavior accurately in order to optimize production design.**
  - minimize cost while maximizing production in a safe and environmentally acceptable way.
- **Predictions of accurate, validated, calibrated computer codes can be used to develop and understand research studies at the microscopic, laboratory, and field scale levels.**
- **TOUGH2 code with Hydrate Module will be used as the cornerstone of the NETL reservoir modeling activities.**

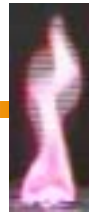


What is TOUGH2?



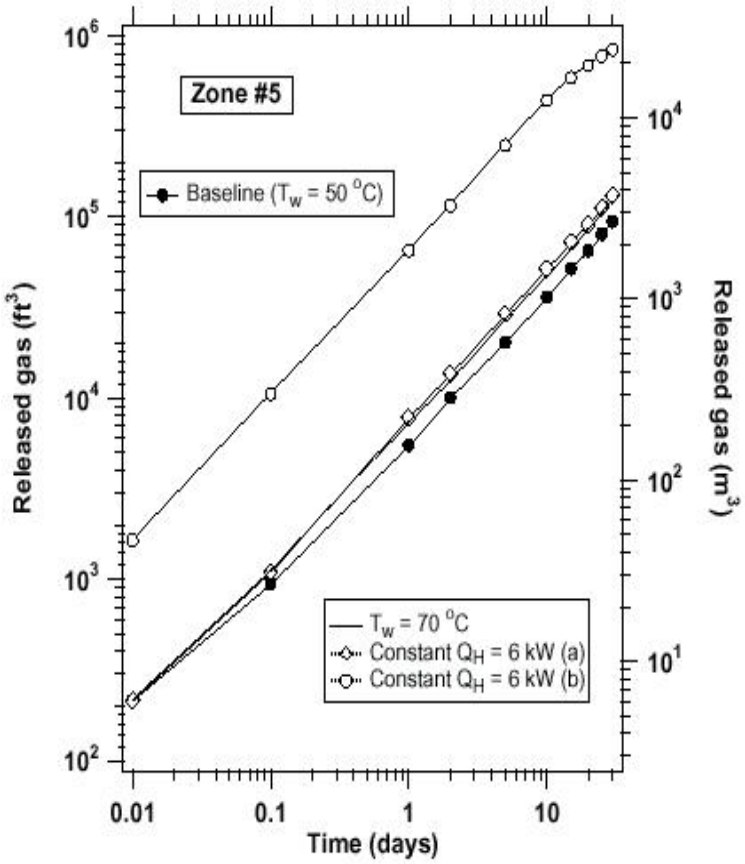


TOUGH2 is a general-purpose numerical simulation program for multi-phase fluid and heat flow in porous and fractured media. It belongs to the MULKOM family of codes, developed in the Earth Sciences Division of Lawrence Berkeley National Laboratory for applications in geothermal reservoir engineering, nuclear waste disposal, and unsaturated zone hydrology.



Reservoir Model Development

Key to Predicting the Behavior of Natural Hydrates

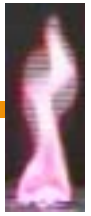


Tough2 simulation of gas production sensitivity to method of heat addition and well boundary conditions; based on data from the Mallik site

- **Obtain the Hydrate Module of TOUGH2 at NETL.**
- **Function as a Beta tester of the Hydrate Module in collaboration with LBL.**
- **Predict what occurs in reservoirs when hydrates in sediments dissociate with TOUGH2/Hydrate Module.**
- **Compare predictions and determine what R&D data is necessary to improve TOUGH2/Hydrate Module.**

Thermal Conductivity Research Background

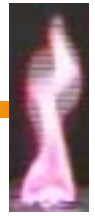
- **The thermal properties of hydrate-bearing sediments strongly influence hydrate decomposition and therefore production.**
  - Number of measurements of thermal properties are several orders of magnitude less than those for phase equilibrium properties.
    - Determining the composition of the system being measured is a major hurdle.
  - Thermal conductivity (TC) is an important parameter in predicting resource production.
    - It is also important in prevention and removal of hydrates during gas production, processing and transportation and in climate calculations.
- **The thermal conductivity of the hydrate-sediment medium is one of the key knowledge gaps in developing gas hydrate simulators for resource recovery (conclusion of the 2001 MBARI Gas Hydrate Workshop).**



Objectives of NETL TC Project

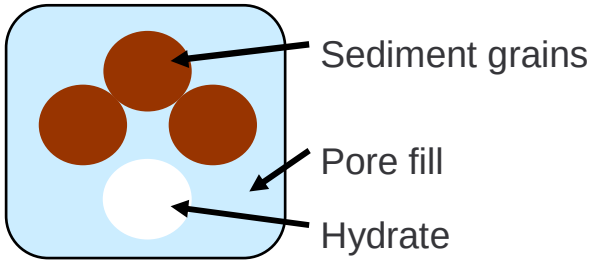
- **Near Term**
  - Develop experimental equipment and procedures to obtain physical and thermal property information on gas hydrate samples of known composition.

- **Long Term**
  - Provide information useful for developing production strategies for gas hydrates from the measurement of important physical, chemical, and thermal properties of carefully prepared and characterized hydrate samples.

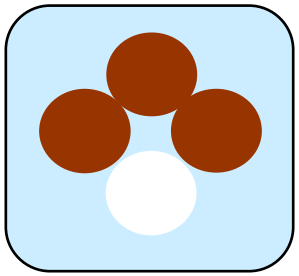


Thermal Conductivity

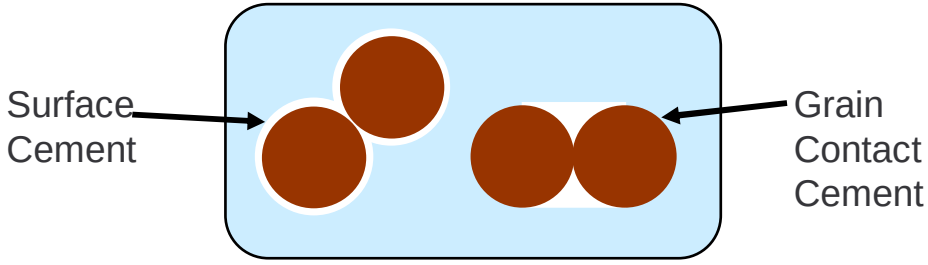
- **The thermal conductivity of an aggregate of sediment, water, and hydrate depends upon:**
  - The conductivity of the individual phases,
  - The concentration and distribution of the phases,
  - The properties of the interfaces between the phases.



Hydrate "floating" in pore space



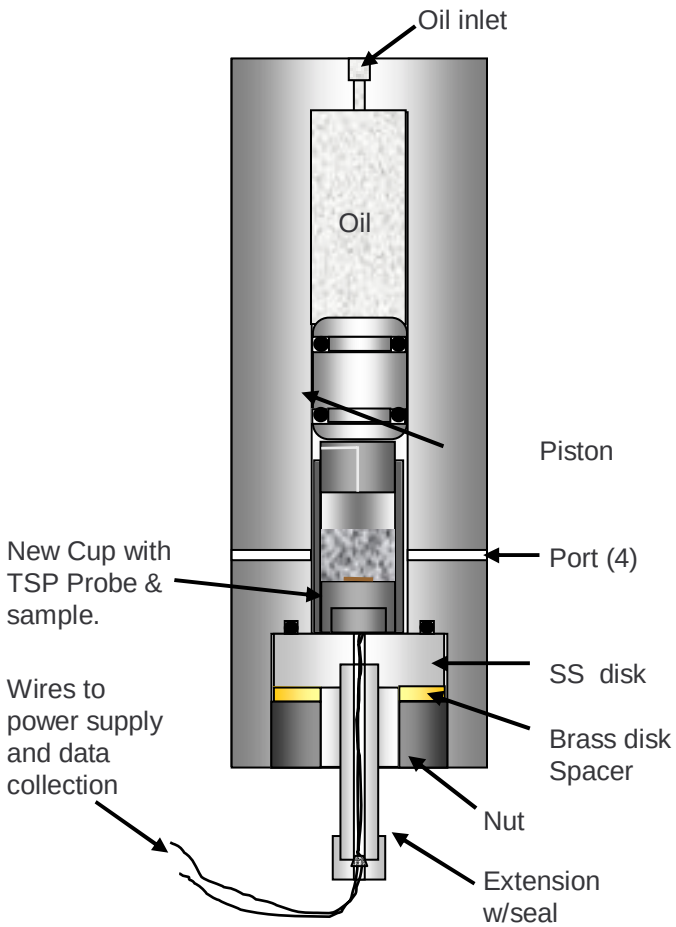
Hydrate replacement of matrix



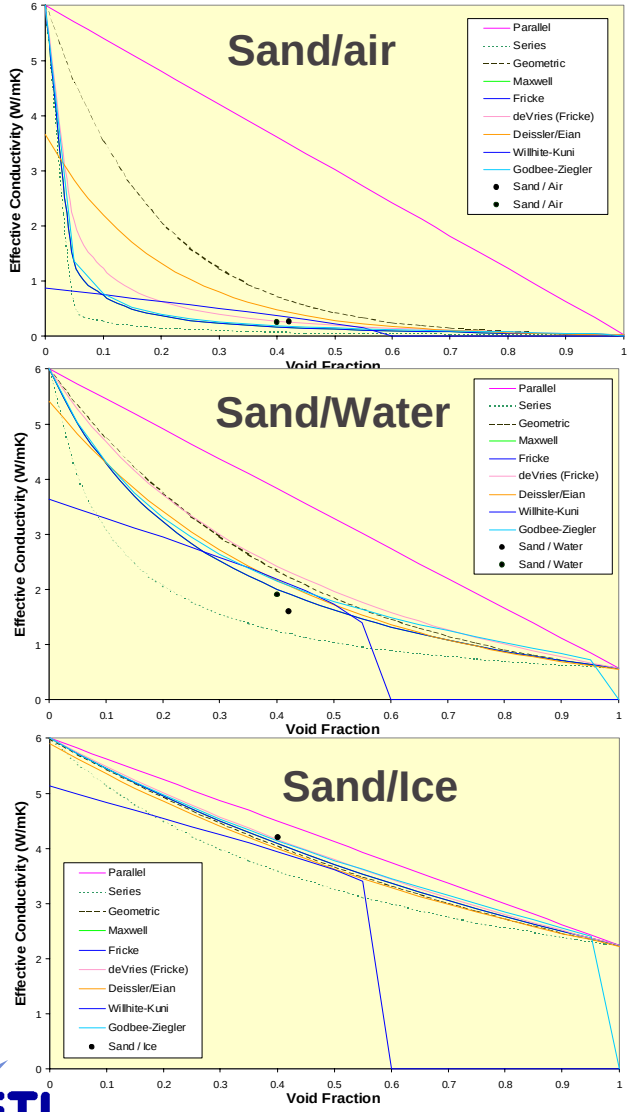
Hydrate cementation between grains

Experimental System for FY03

- **Summary of features of new cup/probe assembly in the HVVC.**
  - Modular cup components.
    - Precision weighing
    - Probe replacement
  - Variable sample capacity.
    - Change sleeve length and cup top insertion length.
  - Verify sample/probe contact.
  - Sample recovery possible.
    - Chamber can be cooled to -30°C.
    - Sample can be pushed out of sleeve.
  - Sample can be compressed.
    - Moveable piston.
    - Cap easily redesigned if required.



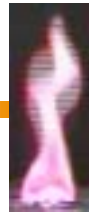
Comparison of Laboratory Data and Model Prediction of Thermal Conductivity



- **TC measurements for ice, hydrate, and water close to expected values.**
- **TC data indicated hydrate decomposition before P-T data.**
- **Some problems were encountered.**
  - Obtaining the TC data was labor intensive.
  - Water migrated outside the sample cup during hydrate decomposition.

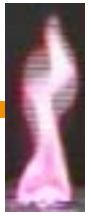
Storage of Methane in Hydrates Background

- **Previous research focused on the conversion of methane in methane hydrates.**
- **During the course of the conversion studies, it was observed that the quantity of methane converted to hydrate varied.**
  - Reaction conditions
  - Physical mixing
  - Additives
- **Preliminary experiments revealed high conversion of methane to hydrates is possible.**

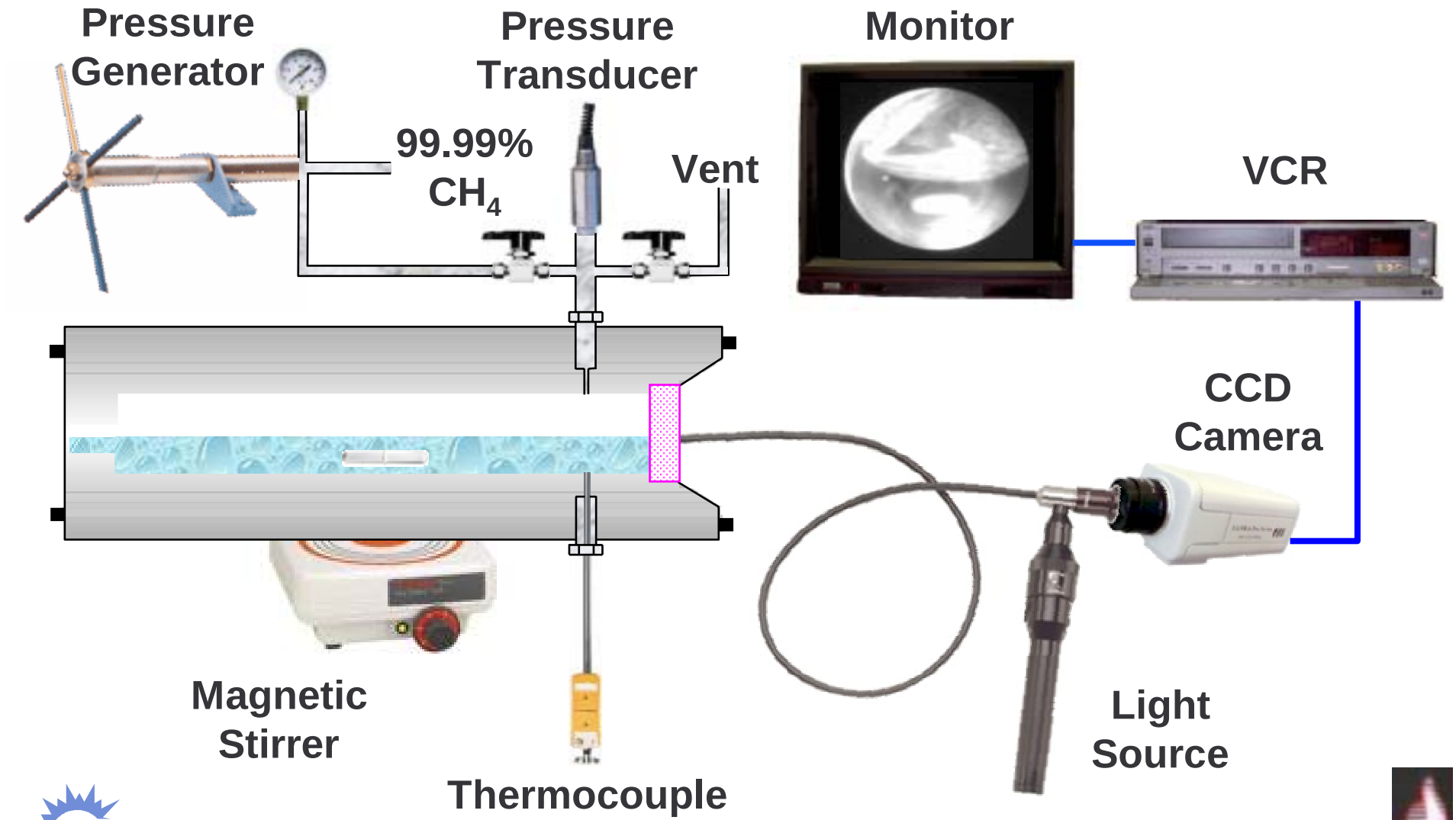


FY-02 Research Plans for the Storage of Methane in Hydrates

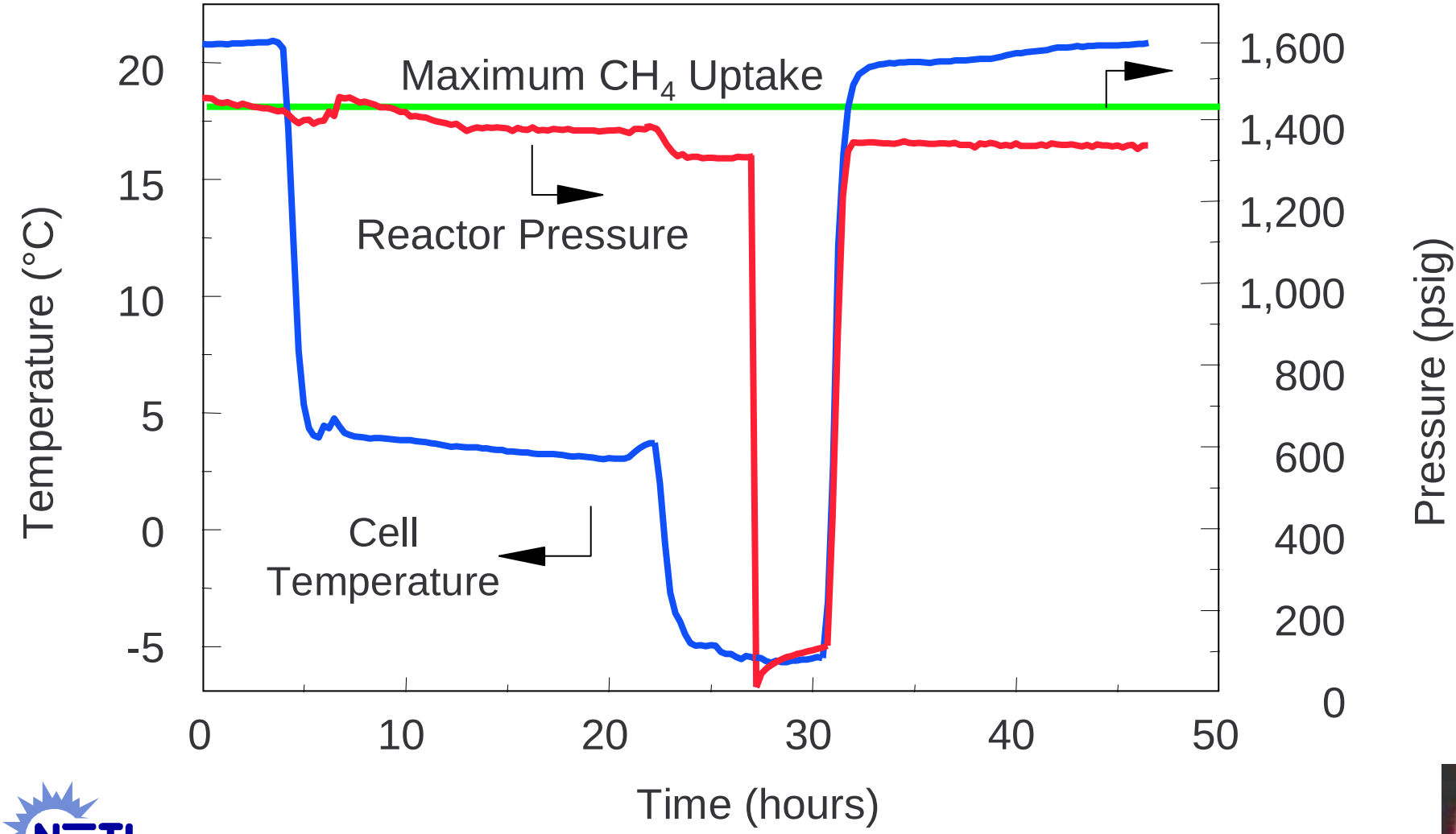
- **Research will focus on methods for forming methane hydrates in the shortest time and with the maximum methane uptake.**
  - The high-pressure view cell currently on hand will be used for preliminary screening studies.
  - Effects of additives, formation rate, etc. will be investigated.
- **A second high-pressure view cell will be constructed.**
- **A large-volume cell will be designed and constructed similar to cells in use at the Naval Research Laboratory and the University of Hawaii.**



High-pressure View Cell Schematic

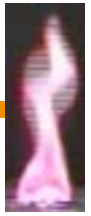


Hydrate Formation Under Constant Methane Pressure (Sodium DodecylSulfate)



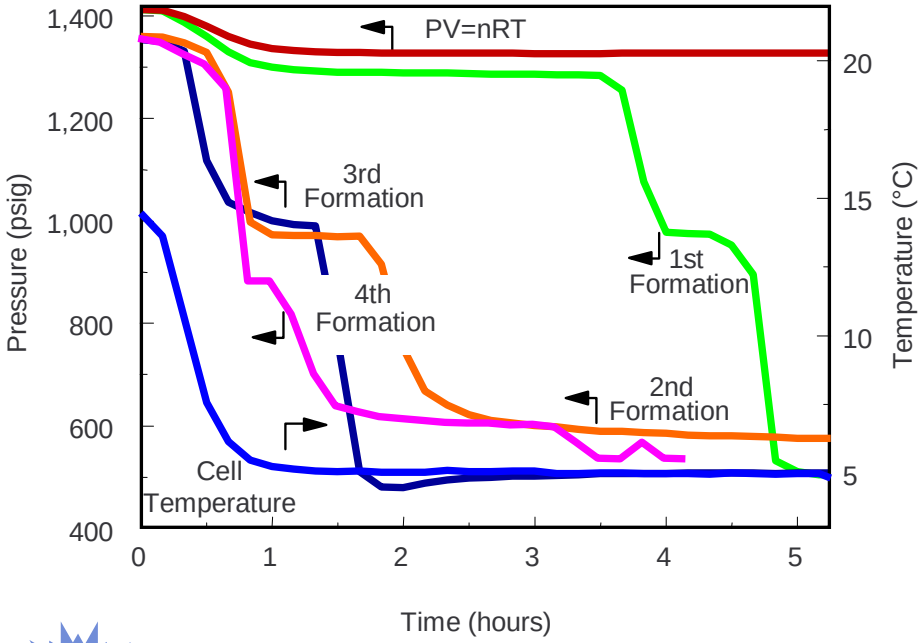
Surfactants Tested for Storage

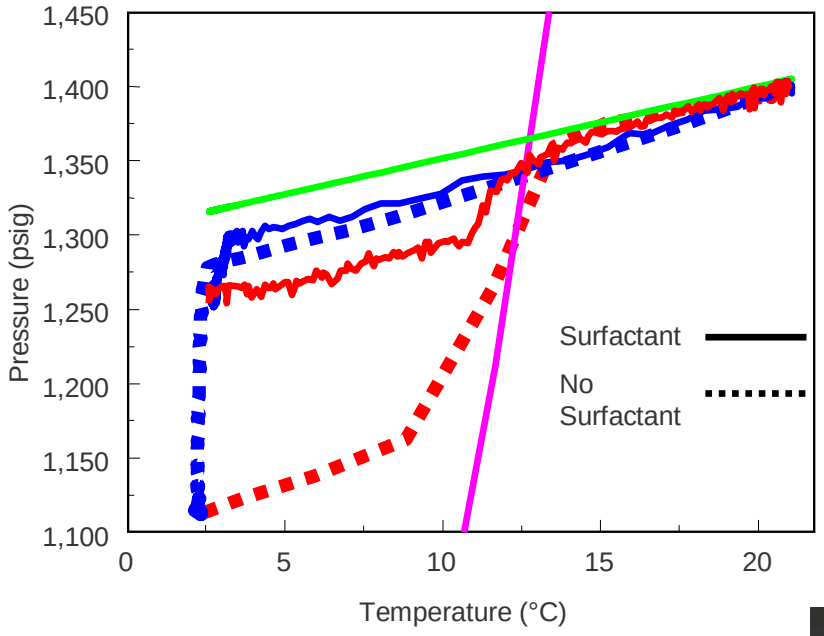
Surfactant	Vent Temperature (°C)	Volume Liquid	% CH_4 Uptake
Sodium Dodecylsulfate	-5.5	15	97.26
Dodecylamine	-10.8	10	9.91
Dodecyl Trimethyl Ammonium Chloride	-15.5	10	13.92
Sodium Lauric Acid	-15.2	10	39.54
Sodium Lauric Acid	-16.1	10	77.35
Sodium Oleate	-13.7	10	70.47
Superfloc 16	-14.0	10	19.59
Superfloc 84	-15.1	10	20.05



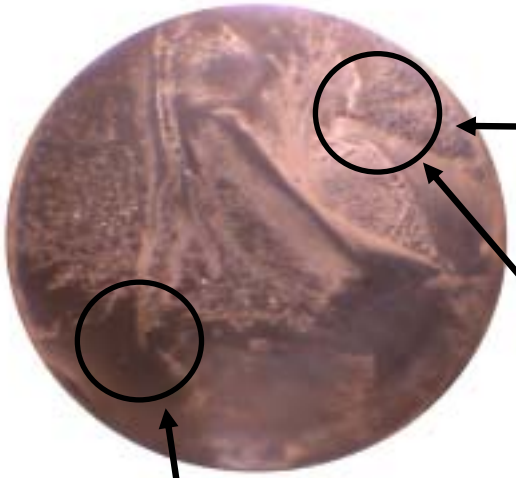
Kinetics of Hydrate Formation/Dissociation

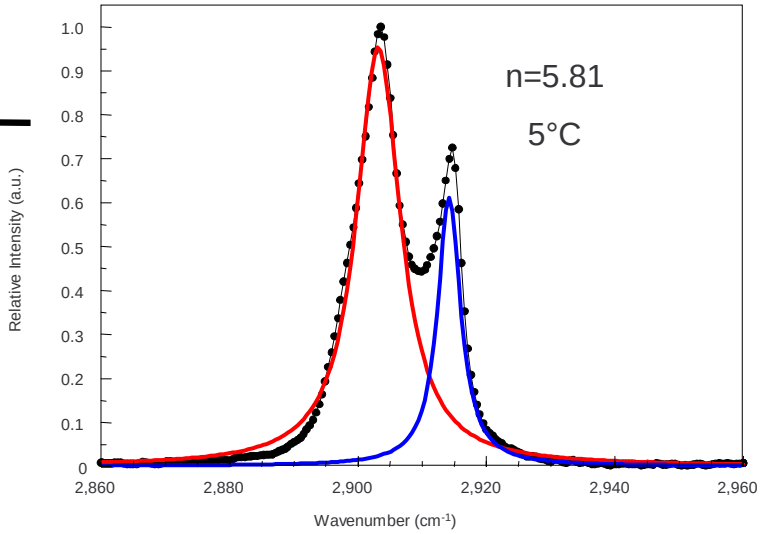
- **Research in collaboration with the Mewbourne School of Petroleum and Geological Engineering Univ. of Oklahoma Performing Kinetic Modeling of Hydrates.**

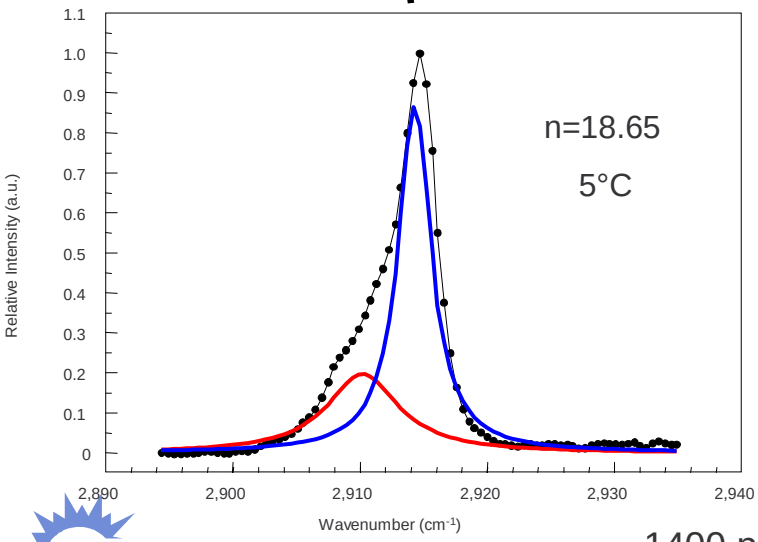


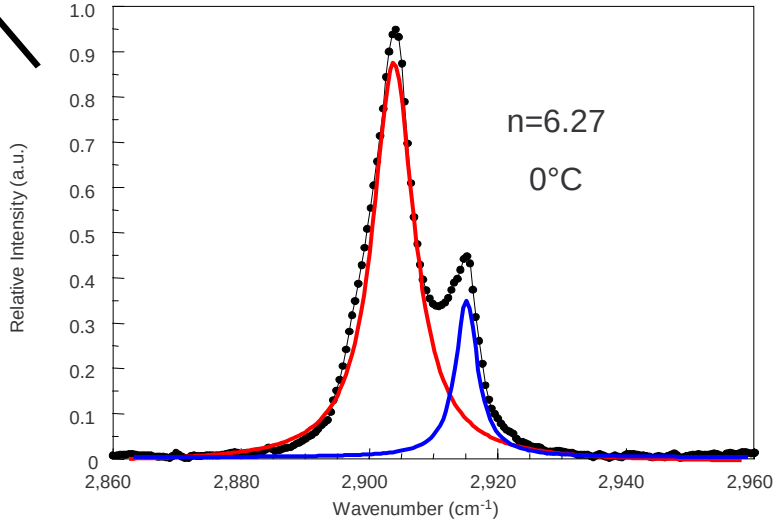


In Situ Raman Spectra of Methane Hydrate Sample

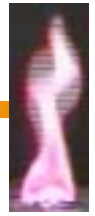






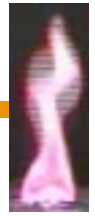


1400 psig, ~61% methane uptake



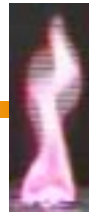
FY-03 Planned Research

- **Continuation of surfactant screening study.**
  - Addition of second view cell to assist in study.
- **Construction of 12.2L hydrate cell.**
  - Most major components on site.
  - Location of unit determined.
  - SARS begun.
  - Study hydrate formation using a NETL-developed ultrasonic technique.
- **Collaborate with Nat. Labs. MH Working Group**
- **Expand associations with U. Oklahoma and U. Hawaii and others.**



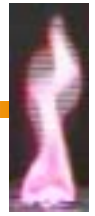
FY-03 Planned Technology Transfer

- **Publication of the article submitted to the Journal *Fluid Phase Equilibrium.***
- **Submission of a second refereed Journal Article on the storage properties of methane in methane hydrates.**
- **A refereed Journal Article on the thermodynamics of hydrate formation and dissociation with University Oklahoma.**



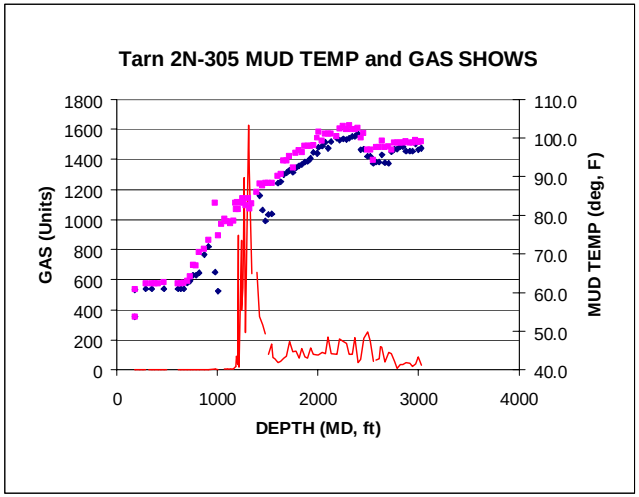
FY-03 Planned Technology Transfer

- Presentation at The Second Workshop of the International Committee on Methane Hydrates, Washington, DC.
- Organize and chair symposium on Gas Hydrates at the 2003 Spring National Meeting of the American Institute of Chemical Engineers in New Orleans, LA.
- Presentation at the symposium on Gas Hydrates at the 2003 Spring National Meeting of the American Institute of Chemical Engineers in New Orleans, LA.



Specialized Mudlogging System

- **In FY-2002, the hardware and software was redesigned to produce a portable device for measuring and recording mud temperatures in extreme climate conditions. The modified system will be tested at a number of drill sites in FY-2003.**



Establish Hydrate Database and Website

Data/Info access seen as essential to R&D success.

- **Need information transfer**
- **Lack of organized GH data/information**
- **Need databank of geophysical and petrophysical data**
- **Need web site for gas hydrate information**

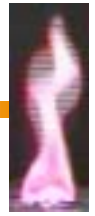
FY02 Progress:

- **Updated digital file of NETL hydrate projects.**
- **Current GIS map coverages of Northern Alaska and Gulf of Mexico data to aid hydrate R&D.**

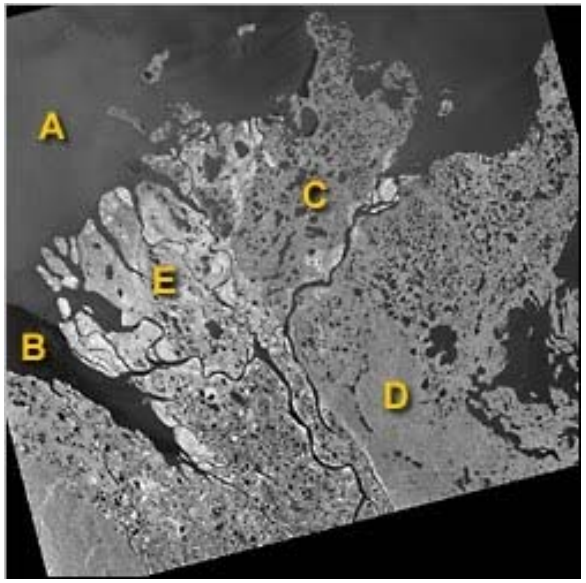
http://www.netl.doe.gov/scng/hydrate/index.html

Mallik Research Consortia

- Geological Survey of Canada, JNOC, JAPEX, GFZ, India, USGS, and NETL.
- Multiple well effort to drill and instrument two monitoring wells and core, log and production test a main research well.
- Deployed the mud temperature system to determine the effects of utilizing mud chillers during the drilling of the main well.
- Funded open hole logging which included NMR logs for better definition of the gas hydrate in the sediments.




ALASKA
YUKON
NORTHWEST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